Temporal and spatial variation in methyl bromide flux from a salt marsh

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[1] Methyl bromide (CH_3Br) is a trace gas involved in stratospheric ozone depletion with both anthropogenic and natural sources. Estimates of natural source strengths are highly uncertain. In this study, >320 highly temporally and spatially resolved measurements of CH_3Br emissions from a salt marsh in Scotland (56°00′N, 2°35′W) were made during one year using eight static enclosures. Net emissions showed both strong seasonal and diurnal cycles. Day-to-day maxima in emissions were associated with sunny days. Emissions dropped to zero when vegetation was removed. Mean measured CH_3Br emission was 350 ng m^{-2} h^{-1}, but a few "hot spots" (measured maximum 4000 ng m^{-2} h^{-1}) dominated integrated emissions. A crude scale-up of the annual mean emission yields an estimate for global CH_3Br emission of ~1 (0.5–3) Gg y^{-1} (range uses annual mean from lowest and highest emitting enclosures), ~10% the global salt marsh emission regularly quoted in the literature.
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1. Introduction

[2] Methyl bromide (CH_3Br) is a trace gas that is emitted into the atmosphere from both natural sources and from commercial production and use. As a consequence of its destructive impact on stratospheric ozone, emissions of CH_3Br from anthropogenic sources (mainly fugitive emissions from crop fumigation) are subject to phase-out under the Montreal Protocol [*World Meteorological Organization*, 2002]. Although the anthropogenic emissions of CH_3Br are relatively well-known, emissions from natural sources, particularly from marine and terrestrial ecosystems, are poorly characterized. This is illustrated by the current global estimates for CH_3Br fluxes in which the sum of estimated sources falls short of the sum of estimated sinks by 59 Gg y^{-1}, with a range of uncertainty in this value spanning −156 to +338 Gg y^{-1} [*Yvon-Lewis*, 2000]. The uncertainties in the natural CH_3Br budget need to be reduced in order to assess better the benefit of anthropogenic emission reduction and to predict any potential effects of future climate and land-use change.

[3] The above data incorporate the estimate, derived from measurements in California, that emissions from salt marshes may contribute almost 10% to total known global sources of CH_3Br [*Rhew et al.*, 2000]. Both biological and non-biological routes of CH_3Br production in soil/plant systems have been proposed. Enzyme-mediated methyl transferase reactions are known to produce methyl halides in some plants [*Saini et al.*, 1995], for example, in rice [*Redeker and Cicerone*, 2004]. The reason for their production is unclear although halide detoxification or by-products of normal metabolism have been suggested [*Manley*, 2002]. Production of methyl halides from abiotic oxidation of organic matter in the presence of halides and Fenton-type catalytic chemistry involving iron has also been demonstrated [*Keppler et al.*, 2000], although rates are an order of magnitude smaller than from biological production. Hence salt marshes, with their relatively high bromide content (from seawater inundation) and organic carbon content, are likely terrestrial ecosystems to study for CH_3Br emissions. Aside from the above-mentioned measurements at two adjacent southern Californian salt marshes [*Rhew et al.*, 2000, 2002; *Bill et al.*, 2002], data on CH_3Br emissions from only two other coastal sites have been published: a coastal wetland in Tasmania [*Cox et al.*, 2004] and a coastal marsh in Ireland [*Dimmer et al.*, 2001] (authors' terminologies are used, but all are assumed to be heavily marine influenced). Published raw data from these studies appears to comprise a relatively small number (a few 10s) of individual temporal and spatial measurements so there remains a paucity of data for CH_3Br emissions from salt marshes. Since emissions are likely to have high spatial and temporal variability, it is important to gather detailed data from different regions and seasons in order to improve the emission flux estimate.

[4] Here we report on a full annual cycle of CH_3Br emissions (including diurnal measurements) from a salt marsh in Scotland (UK). The influence of factors such as temperature, soil properties, water table and vegetation on CH_3Br fluxes was investigated. More than 320 flux measurements were taken between Feb 2005 and Feb 2006. The data set constitutes the most extensive set of CH_3Br fluxes from salt marshes to date.

2. Experimental

[5] Field measurements were carried out using eight enclosure collars permanently installed at a salt marsh on the North Sea coast of Scotland (56°00′N, 2°35′W). The salt marsh is part of a nature reserve and has no other land use. Measurements were made every 1–2 weeks and always between 9:30 and 11:30 am. Diurnal measurements were also made in mid-winter and mid-summer at four of the collars. Enclosure collars were located as four pairs, with the collars in each pair separated by <1 m and intended to act as replicates. Collar pairs 1 + 2 and 3 + 4 were situated

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in an upper, drier area of the salt marsh, while collar pairs 5 + 6 and 7 + 8 were situated in a lower, wetter area. The proportion of drier and wetter areas in the whole salt marsh is approximately equal. All collars were located on vegetated intertidal areas and were subject to inundation by seawater approximately every two weeks. The dominant vegetation in the upper area collars (1–4) was *Aster tripolium*, *Festuca rubra*, and *Spergularia salina*. Representatives of *Triglochin maritimus*, *Plantago maritima*, *Salicornia spec.*, and *Armeria maritima* were also present in the upper area but not in the collars. In contrast, *Plantago maritima* and *Armeria maritima* were the dominant plant species in the lower area collars (5–8), while *Festuca rubra, Salicornia spec.*, and *Spergularia salina* were less common but also found inside the collars. There was no obvious difference in vegetation composition between the four collars in each area. Soil properties were determined from samples taken close to the collars at the start of the measurement period. The soil texture in both areas was a silt loam, subject to saturation. Other soil properties (measured in the upper 10 cm) differed slightly between the two areas: volumetric water content was 74 ± 2.4% and 78 ± 1.1% (mean ± 1 sd of 4 spatial determinations) in the upper and lower areas, respectively, and organic matter content (as determined by loss of ignition at 500°C) was 18.4 ± 0.8% and 21.4 ± 0.1% dry weight, respectively. Water-extractable soil bromide content was determined by ion-chromatography and showed a greater contrast between the upper and lower areas: 80 ± 6 and 95 ± 8 μg g^{-1} dry weight, respectively.

[6] The enclosure collars were opaque PVC tubing (internal diameter 36 cm), buried to at least 5 cm below the surface, and extending 12 cm above ground. When in place, transparent (but UV opaque) Perspex lids enclosed a headspace volume of 0.012 m^3. The lids were used only for the 10 min duration of enclosure so as not to influence vegetation and soil within the collars. Solar intensity, particularly on cloudy days, is not very great at this latitude (56°N), even in summer, so there is negligible increase in internal temperature during the enclosure. After the enclosure, a 400 mL air sample from the headspace was extracted into a 1000 mL gas-tight syringe via a tap in the center of the lid and transferred to a pre-evacuated 1 L Tedlar bag. Sample bags were stored in the dark at room temperature until analysis on the same day or within 24 h. Experiments showed no loss of CH_3Br under these storage conditions.

[7] On each sampling occasion measurements were made of the air and 10 cm soil temperatures, and of the water table level in four perforated tubular wells permanently installed between each pair of collars. The level of sunshine on each visit was also assigned as sunny, broken cloud and sunny periods, or overcast.

[8] Methyl bromide was determined by GC-ECD (HP 5890) using a 30 m long, 0.32 mm i.d. DB624 capillary column (J&W Scientific) with a film thickness of 1.8 μm. The temperature programme was 40°C for 5 min, ramping at 40°C min^{-1} to 240°C and hold for 5 min. 10% methane in argon was used as both the carrier gas (flow 1.3 mL min^{-1}) and as the make-up gas for the ECD (flow 25 mL min^{-1}). A two-trap pre-concentration unit was used prior to GC analysis in order to quantify CH_3Br concentrations to lower than 10 pptv (parts per trillion by volume). The first trap comprised a $^1/_4$-inch stainless steel tube filled with 0.59 g of Tenax, which was Peltier-cooled to −4°C during sample loading to enhance the efficiency of adsorption. The sample was then transferred by heating to the second trap, filled with fine glass beads in 20 cm of $^1/_8$-inch stainless steel tubing, cooled to −79°C using dry ice. Calibration standards in the range 10–1000 pptv were prepared volumetrically in air using a certified 500 ppbv CH_3Br standard in nitrogen (Air Products Inc.). The average analytical relative error in CH_3Br quantification was calculated to be 14%. The detection limit for quantification of net flux was determined by the ability to discriminate a significant difference in CH_3Br concentration between a headspace sample from an enclosure and a sample of ambient air. Based on analysis of the variability of replicates and uncertainty in calibration fits it was estimated that significant difference corresponded to a mixing ratio of 4 pptv, or to an enclosure net flux of 14 ng CH_3Br m^{-2} h^{-1}.

3. Results

3.1. Measurements of CH_3Br Flux

[9] The time series of CH_3Br emissions from each collar are shown in Figure 1. All collars were net emitters of CH_3Br except for some which had zero net emissions during the winter period, Dec–Feb. No net uptake of CH_3Br was ever measured. A clear annual cycle of increased emissions in summer compared with winter is apparent for all eight collars. The seasonal "amplitude" between average summer emissions (mid-March to mid-September) and average winter emissions was in the range ~2–5 fold.

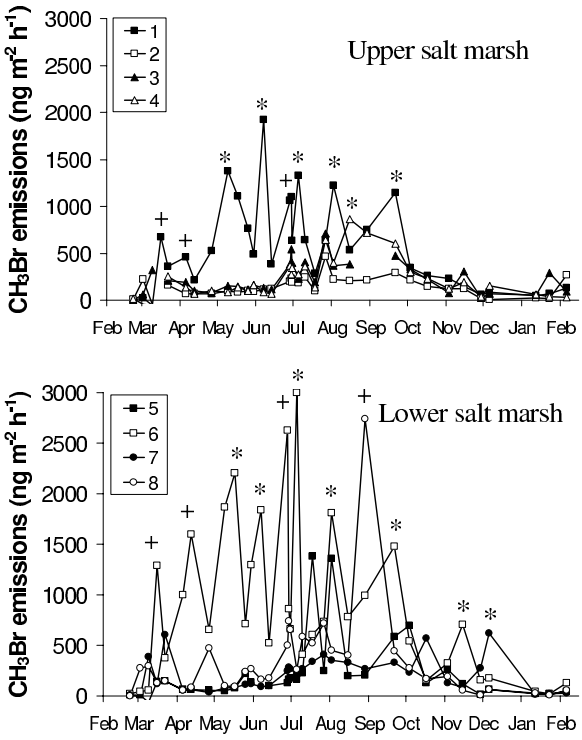

Figure 1. CH_3Br emissions between Feb 2005 and Feb 2006 from eight collars situated in upper and lower salt marsh. The asterisks and crosses illustrate that major peaks in CH_3Br emissions occurred on days classified as sunny, or sunny periods, respectively.

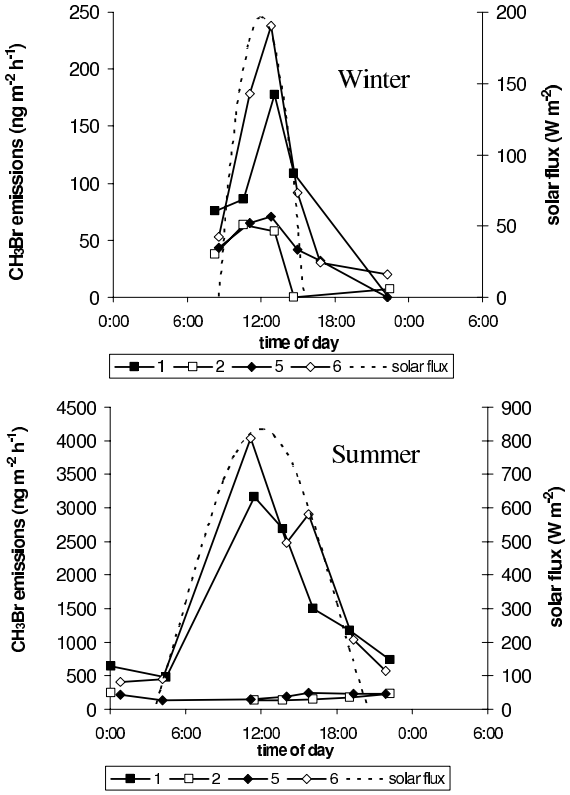

Figure 2. Diurnal variation in CH_3Br emissions from four collars (one pair each from the upper and lower areas) in summer (10 Jul 2005) and winter (6 Dec 2005). Note that y-axis scales are different. The dashed line is the calculated theoretical clear-skies total solar flux for sampling location and day.

(The average summer enhancement across all eight collars was ~3 fold). Elevated emissions from a salt marsh during the growing season (defined by the authors as March–September) were similarly reported by *Rhew et al.* [2000]. Variation in CH_3Br emissions was larger between individual collars in different pairs at the same area (upper or lower) than between the two areas. Thus designated replicate collars clearly did not demonstrate replicate behavior in practice. In particular, in each area of the salt marsh there was one collar which emitted significantly more than the others (collar 1 in the upper area and collar 6 in the lower area). The fluxes of CH_3Br from these collars were persistently larger, particularly during March to September, although other collars also showed periods of enhanced emissions. The two highest-emitting collars (1 and 6) also showed the largest annual variation.

[10] Figure 2 shows there was also a strong diurnal variation in CH_3Br emissions from the higher-emitting collars, and smaller (or no) diurnal variation in emissions from the lower-emitting collars, in both mid-summer and mid-winter. The emissions in winter were an order of magnitude lower than in summer, and the width of the cycle was much narrower, corresponding to the substantially smaller number of daylight hours. Although emissions were significantly lower at night, it is important to note they did not cease completely. The diurnal variations in emission from high-emitting collars match closely the shape of the corresponding calculated theoretical maximum (clear-skies) total solar flux for this latitude and Julian Day of sampling. Temperature variation during the day could not account for the variation in emission. There was only a modest positive correlation between CH_3Br emissions from a given collar and the soil or air temperature (Figure 3). *Dimmer et al.* [2001] similarly found strong diurnal cycles of methyl halide emissions, but only little variation in temperature (3–4°C), again suggesting a stronger association with light than with temperature. These observations contrast with those of *Rhew et al.* [2002] who reported emission rates being strongly correlated to diurnal air temperature.

[11] There was also a strong association between sunshine conditions and the timings of peaks in CH_3Br emissions from the high emitting collars above the general annual trend. The majority of the peaks in CH_3Br emission occurred on days classified as sunny (marked by the asterisks on Figure 1). The remainder occurred on days classified as sunny periods (marked by crosses on Figure 1). None of the peaks occurred on overcast or precipitating days. Since sampling was systematically undertaken at mid morning, before the mid-day peak, the between-day and between-collar variation of emissions in Figure 1 is not an artefact of sampling at different times during the diurnal cycle. This is illustrated by the fact that the peak emission measured during the summer diurnal measurement (Figure 2, bottom) was greater than the emissions measured at mid morning in the routine time series around this time (Figure 1). Thus maximum emissions from the flux collars are expected to be higher than those shown in the time series graphs.

[12] The apparent association of CH_3Br emission with vegetation suggested by the strong diurnal and seasonal cycles and the association with sunny conditions was further supported by an experiment in May–June 2005 in which measurements were made before and after vegetation was removed from a separate enclosure collar (Figure 4), located close to collars 1 and 2 in the upper area. Baseline monitoring of this additional collar for three weeks showed that its emissions were in the same range as from the lower-emitting collars in the main study, but dropped to zero and subsequently even slightly negative after all surface vegetation in the collar was removed. This is in good agreement with experiments by *White et al.* [2005] who also found CH_3Br consumption after vegetation removal in peatlands.

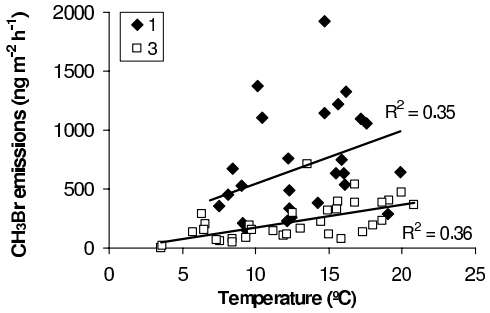

Figure 3. Example scatterplots of CH_3Br emissions from two different collars with either soil temperature (collar 1) or air temperature (collar 3), for the entire year of measurements.

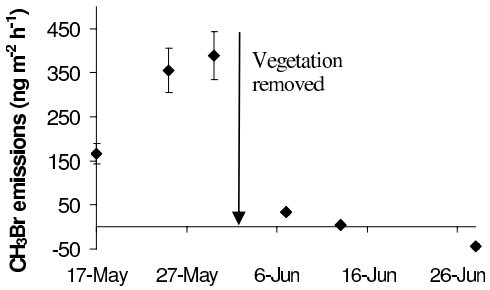

Figure 4. Vegetation removal experiment in May/June 2005. After baseline measurements of CH_3Br emissions, all vegetation was removed from an additional collar located in the upper salt marsh and emission measurements continued. Error bars correspond to the ±14% relative error estimated for the GC analytical measurement of CH_3Br concentration.

Overall, it appears that processes associated with vegetation are the dominant source of CH_3Br emissions, as noted previously for *Brassica* [*Gan et al.*, 1998], salt marsh [*Rhew et al.*, 2002], rice plants [*Redeker et al.*, 2003] and, recently, for tropical ferns [*Saito and Yokouchi*, 2006].

[13] Mean annual emissions were slightly greater from the lower salt marsh area than from the higher area (~400 and 300 ng m^{-2} h^{-1}, respectively) which is likely associated with the higher soil bromide content at the former. However, the difference between these averages is small compared with the large variations between enclosures within a salt marsh area. There was no obvious explanation for these "hot spots" attributable to soil properties measured or plant species enclosed. This contrasts with *Rhew et al.* [2000], who related spatial variability in emissions to the different vegetation zones of the Californian salt marsh studied. There was also no association between CH_3Br emissions and water table depth.

3.2. Comparison to Other Salt Marsh Studies and Global Implementation

[14] Despite the high spatial variability shown in this work, it is useful to compare the approximate magnitude of net CH_3Br emissions from this salt marsh in Scotland with those previously reported. The unweighted mean and median daytime CH_3Br emissions over the whole year and all eight collars (n = 324 measurements) were 350 and 190 ng m^{-2} h^{-1}, respectively. Emissions from two collars regularly exceeded 600 ng m^{-2} h^{-1} during the growing season, and the highest emission measured (in the middle of a day in July) reached 4000 ng m^{-2} h^{-1}. These emission magnitudes are in the same general range as those reported from coastal marshes in Ireland [*Dimmer et al.*, 2001] and Tasmania [*Cox et al.*, 2004]. Although *Dimmer et al.* [2001] did not provide detail on individual flux measurements, they reported an average daytime flux of 28 (range 8–44) × 10^{-4} g m^{-2} y^{-1} (based on 26 measurements), which corresponds to an average daytime flux of 320 (range 90–500) ng m^{-2} h^{-1}. The average daytime flux reported by *Cox et al.* [2004] in Tasmania was 190 (range 27–470) ng m^{-2} h^{-1}, derived from 10 individual measurements. In contrast, the global annual salt marsh CH_3Br flux quoted by *Rhew et al.* [2000] corresponds to an average emission flux of 4200 ng m^{-2} h^{-1} for the Californian salt marsh on which their annual estimate is derived. This flux is about an order of magnitude larger than our measurements and those of *Dimmer et al.* [2001] and *Cox et al.* [2004], and may reflect the higher temperatures and solar flux at their lower latitude location. However, the range of flux measurements (n = 36) reported by *Rhew et al.* [2000] was very large (between 13 and 160,000 ng m^{-2} h^{-1}) and it is not clear how this variability was handled in the scaling up. Many of their reported individual emission measurements were of the order of a few hundred ng m^{-2} h^{-1} and thus comparable to those reported here. It is possible, therefore, that the global CH_3Br emission estimate for salt marshes provided by *Rhew et al.* [2000] reflects an upper limit. Crudely scaling up our annual mean CH_3Br emission of 350 ng m^{-2} h^{-1} to a global salt marsh area of 0.38 × 10^{12} m^2 [*Woodwell et al.*, 1973] yields an estimate for global emission of ~1 Gg y^{-1}. To account for variability, scaling up the annual means of the lowest and highest emitting of the 8 collars yields a range in estimated global emission of ~0.5 to ~3 Gg y^{-1}. The mean global emission from this work is ~10% of the *Rhew et al.* [2000] global salt marsh emission estimate usually quoted in the methyl bromide literature.

4. Conclusions

[15] Net emissions of CH_3Br from salt marshes appear to be strongly associated with the vegetation. Although seasonal variation in emission followed the trend of seasonal variation in temperature this is presumably due to plant-related processes as there was only a modest correlation between day-to-day emission and air or soil temperature. In contrast, diurnal variations of emissions were strongly associated with the solar cycle with highest emissions in the middle of the day and lowest emissions during the dark. Also, observed peaks in CH_3Br emission always occurred under sunny conditions. Hence the diurnal and day-to-day variation in sunshine appears to have more direct influence on high emissions than temperature, at least at this relatively high latitude site.

[16] Salt marsh CH_3Br emissions are also highly spatially variable, with a small proportion of "hot spots" accounting for the bulk of the spatially-integrated net emissions. There was no obvious explanation for the spatial heterogeneity of CH_3Br emissions on account of plant species or measured soil properties, apart from a small association of greater average emission with greater soil bromide content.

[17] CH_3Br emissions estimates from salt marshes have been shown to be strongly dependent on the location, season and time of day at which the underpinning measurements are made. Indeed, this work has shown that emissions from a few "hot spots" are likely to contribute the majority of integrated area emissions. This leads to obvious difficulties in global scaling up. Whilst temporal variability of emissions can be parameterized in terms of temperature and sunlight, spatial variation can only be accounted for by direct measurement. This study presents a full annual cycle of measurements which should provide the best estimate of annual emissions without recourse to weighting as compared with short-period measurements. A crude scaling up of the annual mean CH_3Br emission of 350 ng m^{-2} h^{-1} obtained in this work yields an estimate for global emission

of ~1 (0.5–3) Gg y^{-1}, or ~10% of the global salt marsh emission estimate regularly quoted in the methyl bromide literature.

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